



CO₂ Capture at High Temperature and Low Concentration on Li₄SiO₄ Based Sorbents

Monica Puccini*, Maurizia Seggiani, Sandra Vitolo

Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 1, 56122 Pisa, Italy
 m.puccini@diccism.unipi.it

Solid sorbents based on lithium orthosilicate (Li₄SiO₄) have shown promise for CO₂ capture at high temperature. Improved sorption properties can be obtained by appropriate doping. In this study, different promoted Li₄SiO₄-based sorbents were prepared by addition of potassium carbonate and binary/ternary alkali (Li, K and Na) carbonate eutectic mixtures. The CO₂ sorption properties of the sorbents were investigated by thermal gravimetric analysis (TGA) at different temperatures in the range between 500 and 600 °C and at low CO₂ partial pressure (0.04 atm). The results showed that all the promoters used noticeably improved the CO₂ sorption capacity in comparison to no-promoted Li₄SiO₄. At the optimum sorption temperature of 580 °C, Li₄SiO₄ with addition of 30 wt% of K₂CO₃ showed the best CO₂ adsorption properties with sorption capacities of 230 mg CO₂/g sorbent corresponding to a conversion of about 80 %. Besides this sample maintained its original capacity during multiple CO₂ sorption/desorption cycles.

1. Introduction

Carbon dioxide (CO₂) is considered one of the most important greenhouse gases (GHG) among the anthropogenic emissions into the atmosphere due to the dependence of world economies on fossil fuels as energy source. Approximately 85 % of world energy demand is supplied by fossil fuels (Yang et al., 2008), which results in the emission of about 23·10⁹ tonnes CO₂/year (Pires et al., 2011). One approach that holds great promise for reducing GHG emissions is carbon capture and sequestration (CCS). Under this concept, CO₂ would be captured from large point source, such as power plants and refineries, and injected into geological formations (depleted oil and gas fields, saline formations, unmineable coal seams) (Soundararajan and Gundersen, 2012).

Among the technologies for CO₂ capture from flue gases, the absorption process using aqueous solution of monoethanolamine (MEA) is the most common and available for industrial applications (Chavez and Guadarrama, 2011). But, the significant energy penalty due to the low operating temperatures (40-150 °C) and the high regeneration energy requirements represent important limitations for its application (White et al. 2003). The flue gases produced after the combustion of fossil fuels in a turbine are usually in the temperature range from 700 to 900 K (Ochoa-Fernández et al., 2006). Consequently, they need to be cooled to the temperature levels required for the absorption process in case a wet-absorption method is chosen for separation. Thus, in recent years emerging technologies operating at high temperature (450-750 °C) are being investigated as alternatives to low-temperature CO₂ capture systems.

A promising approach consists in using suitable metal-oxide based inorganic sorbents that reversibly react with CO₂ at elevated temperature (Wang et al., 2010). Materials containing lithium zirconate (Li₂ZrO₃) and lithium orthosilicate (Li₄SiO₄) seem to be promising CO₂ acceptors in the range of 500-700 °C (Pannocchia et al., 2007). Main advantages of these materials are their high CO₂ capture capacity, lower regeneration temperatures (< 750 °C) compared to other high-temperature sorbents, such as CaO, and their excellent stability that allow operation over a significant number of cycles without losing their sorption capacity. Kato et al. (2005) investigating the CO₂ adsorption properties of Li₂ZrO₃ and Li₄SiO₄ pellets at low CO₂ concentration (500 ppv – 20 vol%) concluded that the CO₂ adsorption on Li₄SiO₄ is more than 30 times faster than that on Li₂ZrO₃ at the same sorption conditions. Furthermore, Li₄SiO₄ shows lower costs of the raw materials involved comparing the expensive ZrO₂ with cheaper SiO₂.

For these reasons, Li_4SiO_4 is considered one of the most promising candidates for the post-combustion CO_2 capture at high temperature and low CO_2 concentrations (following the reaction: $\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3$). Lithium orthosilicate can theoretically adsorb CO_2 in amounts up to 0.36 g CO_2 /g sorbent. In practice, CO_2 capacities up to 35 wt% have been reported at a temperature of 700 °C in pure CO_2 (Kato et al., 2005). Considering the potential applications of these sorbents for carbon dioxide capture from exhaust gas in thermal power plants (low CO_2 concentrations) or for the in situ removal of CO_2 produced in some reactions such as water gas shift (WGS) reaction and steam-methane reforming (SMR), the requested temperature range is between 450 and 600 °C. At these temperatures, kinetic limitations during CO_2 adsorption are still the main obstacle for application of Li_4SiO_4 .

For this reason, various doping methods have been proposed to improve the Li_4SiO_4 reactivity (Seggiani et al., 2011). Different alkali carbonates dispersed in Li_4SiO_4 have been proposed as promoters since such carbonates forms eutectic mixtures with product Li_2CO_3 that melt at high temperatures (> 500 °C) (Seggiani et al., 2013). According to the double shell model proposed for the CO_2 adsorption mechanism on Li_4SiO_4 (Kato et al., 2002), the resultant molten carbonate shell greatly facilitates CO_2 diffusion throughout the product layer compared to the solid Li_2CO_3 shell in pure Li_4SiO_4 case. The objective of this work was the development of novel promoted Li_4SiO_4 based sorbents for CO_2 capture at high temperature and low CO_2 concentration by addition of alkali carbonate mixtures. Different promoted Li_4SiO_4 -based sorbents were prepared by addition of potassium carbonate and binary/ternary alkali (Li, K and Na) carbonate eutectic mixtures. The promoters were added in several amounts (10, 20 and 30 wt%) to pure Li_4SiO_4 powders synthesized by solid state reaction using crystalline silica. Their CO_2 sorption properties were investigated by thermal gravimetric analysis (TGA) at different temperatures in the range between 500 and 600 °C and at low CO_2 partial pressure (0.04 atm). In addition, the cyclic stability of the selected samples were investigated by carrying out 25 cycles of CO_2 sorption/desorption.

2. Experimental

2.1 Sorbents preparation and characterization

Li_4SiO_4 powders were prepared by the solid state method. Starting materials were reagent-grade Li_2CO_3 and ZrO_2 (from Sigma-Aldrich) in a 2:1 molar ratio. The materials were weighed, mixed, and ground in an agate mortar with a suitable amount of water. Then, the mixtures were dried and calcined in air at 900 °C for 4 h. Both temperature increase and decrease ramping rates were set to 60 °C/h. The resulting powders were ground by agate mortar to break down any agglomeration and then sieved to produce Li_4SiO_4 particles with size below 10 μm . Li_4SiO_4 -based sorbents were prepared mixing 10, 20, 30 wt% of potassium carbonate (K_2CO_3), binary ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$) and ternary ($\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{Na}_2\text{CO}_3$) eutectic carbonate mixtures with the previously synthesized pure Li_4SiO_4 powder. Table 1 shows the composition and melting points of the binary and ternary eutectic mixtures used in this study.

Powder X-ray diffraction (XRD) characterization of pure and promoted Li_4SiO_4 samples prior to and after CO_2 sorption was conducted using a Philips PW 1050/25 X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The XRD patterns were recorded over a 2θ range between 10° and 70°. Phase identification was verified by comparison against the corresponding Joint Committee Powder Diffraction Standards (JCPDS).

A JEOL 5600 LV scanning electron microscope (SEM) was used to observe the morphology and the promoter distribution in the samples.

2.2 Experimental procedure

Carbon dioxide adsorption on prepared powders was studied using a thermogravimetric analyser (TGA Q500 TA Instrument). About 20 mg of sample were placed in a sample pan and, prior to CO_2 sorption testing, the sample was pre-conditioned and dried in a nitrogen flow (100 mL/min) elevating the temperature (at 10 °C/min) to the operating temperature, till sample weight became stable. Then, the N_2 flow was switched to a mixture CO_2/N_2 containing 4 vol% of CO_2 . The total feed gas flow rate was maintained at 100 mL/min at atmospheric pressure. The weight increase due to CO_2 sorption was recorded as a function of time during the adsorption process lasted 120 min. Besides, to assess the stability of the optimized sorbent twenty-five adsorption/desorption cycles were carried out. The adsorption of CO_2 was carried for 60 min at the desired temperature in 4 vol% CO_2 flow. Afterwards, the feed gas stream was switched to a pure N_2 flow (100 mL/min) and the temperature was raised to 700°C with heating rate of 20°C/min. The sample was kept to the regeneration temperature until it was completely regenerated. The regeneration process lasted about 15 min. After that, a new cycle was carried out.

Table 1. Composition and melting point of binary and ternary eutectic mixtures used as promoters.

Eutectic composition (mol %) ^a	Melting point (°C) ^a
Li ₂ CO ₃ (42.7 %) / K ₂ CO ₃ (57.3 %)	498
Li ₂ CO ₃ (42.5 %) / K ₂ CO ₃ (26.8 %) / Na ₂ CO ₃ (30.6 %)	393

^a Data extracted from NSRDS (1978).

3. Results and discussion

In order to establish the optimum CO₂ sorption temperature, preliminary sorption runs were performed on the pure and some doped Li₄SiO₄ samples at temperatures between 500 and 600 °C. As an example, Figure 1 shows the weight increase of the Li₄SiO₄ with addition of 20 wt% K₂CO₃ as a result of CO₂ sorption from a 4 vol% CO₂ stream at temperatures between 500-590 °C. As can be seen, the CO₂ sorption capacity increases with the temperature between 500 and 580 °C and then decreases at higher temperatures. The same behaviour was observed for the other samples showing that the maximum adsorption of CO₂ after 2 h was reached at 580 °C. This is attributed to the equilibrium temperature of Li₄SiO₄ that was calculated to be about 590 °C at the CO₂ partial pressure of 4.04 kPa (4 vol% CO₂ at a total pressure of 101 kPa).

Since the promoters showed no affinity for the CO₂ capture but contributed to the sorbent weight, the conversion of Li₄SiO₄, $X_{\text{Li}_4\text{SiO}_4}$, was used to assess and compare the effect of the different promoters used on the CO₂ sorption reaction. The percentage conversion $X_{\text{Li}_4\text{SiO}_4}$ was calculated by using the equation (1):

$$X_{\text{Li}_4\text{SiO}_4} (\%) = \frac{\Delta W}{F_{\text{Li}_4\text{SiO}_4} \cdot r_s} \quad (1)$$

where ΔW is the percentage weight change of the sorbent during the adsorption, $F_{\text{Li}_4\text{SiO}_4}$ is the weight fraction of Li₄SiO₄ in the sorbent and r_s is the stoichiometric uptake of CO₂ by Li₄SiO₄, which is about 0.36 g of CO₂/g of Li₄SiO₄. For each series of promoted samples, the CO₂ sorption rate generally increases as a function of the promoter amount added (see Table 2). This can be attributed to a more efficient distribution of promoter over the surface of the Li₄SiO₄ particles. As shown, the addition of 30 wt% K₂CO₃ to pure Li₄SiO₄ powders produced a sorbent which exhibited the best CO₂ adsorption performance in terms of sorption capacity: the adsorbed amount of CO₂ after 2 hours was nearly 23 wt% of the starting material corresponding to a 80% conversion of Li₄SiO₄. Besides, the sorption capacity of the samples prepared by addition of potassium carbonate are higher than those of sorbents prepared with the relative binary/ternary eutectic carbonate mixtures. These results can be related to the formation of a liquid phase of Li-K carbonates occurred on the surface of Li₄SiO₄ particles during the carbonation reaction that reduces CO₂ diffusion resistance to the solid product Li₂CO₃ shell in pure Li₄SiO₄ (Ida and Lin, 2003). While, for the Li-K and Li-K-Na samples a eutectic liquid phase is already present at the start of CO₂ sorption.

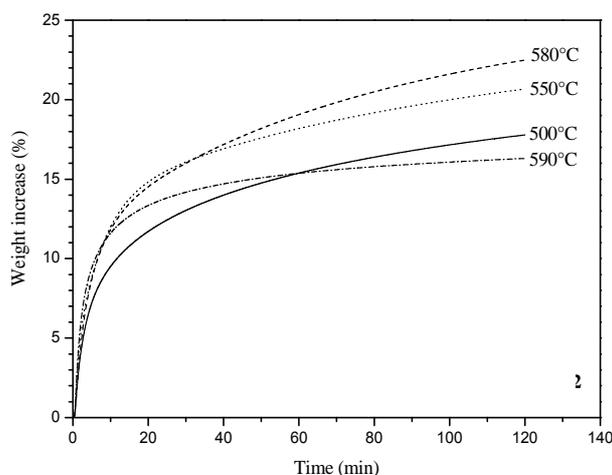


Figure 1: CO₂ sorption profiles on the sorbent with 20 wt% K₂CO₃ added, in 4 vol% CO₂ stream at different temperatures.

Table 2. Percentage conversion of Li_4SiO_4 .

Promoter	10%	20%	30%
K_2CO_3	57.5	75.0	81.4
$\text{Li}_2\text{CO}_3 / \text{K}_2\text{CO}_3$	44.6	72.0	75.3
$\text{Li}_2\text{CO}_3 / \text{K}_2\text{CO}_3 / \text{Na}_2\text{CO}_3$	57.0	67.4	69.6

As example, the SEM images of the Li_4SiO_4 sorbent doped with 30 wt% of K_2CO_3 and 30 wt% of $\text{K}_2\text{CO}_3/\text{Li}_2\text{CO}_3$ eutectic mixture quenched at 580°C in N_2 before CO_2 sorption are reported in Figure 2. As can be seen, the sample with 30 wt% of K_2CO_3 shows the same morphology (Figure 2b) of the starting Li_4SiO_4 powder (Figure 2a), i.e. porous agglomerates of dense particles with submicron particles of K_2CO_3 dispersed on the particle surfaces. Whereas, dense particle agglomerates with average size of $50\ \mu\text{m}$ were observed in the sample with 30 wt% of $\text{K}_2\text{CO}_3/\text{Li}_2\text{CO}_3$ (Figure 2d). This is attributed to the fusion of the eutectic mixture on Li_4SiO_4 particles during the heating in N_2 to the adsorption temperature (580°C) greater than the reported melting point (498°C). The presence of these large agglomerates with dense morphology allowed to reduce the interface surface for the reaction between gaseous CO_2 and sorbent particles with consequent reduction in CO_2 uptake. In addition, the diffusion of CO_2 through the molten layer of eutectic mixture before reaching the Li_4SiO_4 particle surface may represent an additional diffusional resistance. Figure 3 shows, by means of X-ray analysis, the microstructure changes of the 30 wt% K_2CO_3 doped Li_4SiO_4 before and during CO_2 sorption and after CO_2 desorption. Compared to XRD pattern of the original sorbent (top of Figure 3), XRD pattern of the sorption product (middle of Figure 3) shows that the peaks assigned to Li_4SiO_4 disappeared and that the peaks associated with Li_2CO_3 and Li_2SiO_3 are present instead. This result indicates that during the CO_2 sorption process Li_4SiO_4 reacts with CO_2 to become Li_2CO_3 and Li_2SiO_3 . XRD pattern of the regenerated sorbent (bottom of Figure 3) only shows peaks assigned to Li_4SiO_4 : this means that, after CO_2 desorption, Li_2CO_3 and Li_2SiO_3 react to produce again Li_4SiO_4 by releasing CO_2 .

The cyclic stability of the Li_4SiO_4 sorbent doped with 30 wt % of K_2CO_3 was investigated by carrying out 25 cycles of CO_2 sorption/desorption (Figure 4). At the end of the first regeneration, a mass loss of about 4% compared to the initial weight of the sample (after preconditioning) was observed. This behaviour can be attributed to the completion of release of bound water from the sorbent. This weight loss justifies the apparent CO_2 sorption capacity loss registered in the second adsorption run. After the first cycle, the CO_2 absorption capacity and capture-regeneration rate remained essentially constant during the subsequent cycles, implying excellent stability. SEM images of one-cycle and twenty-five cycles used sample (Figure 5) shows that the morphology of the sorbent did not change after 25 CO_2 capture-regeneration cycles, supporting the good regenerability properties evidenced by the CO_2 capture/regeneration cycles.

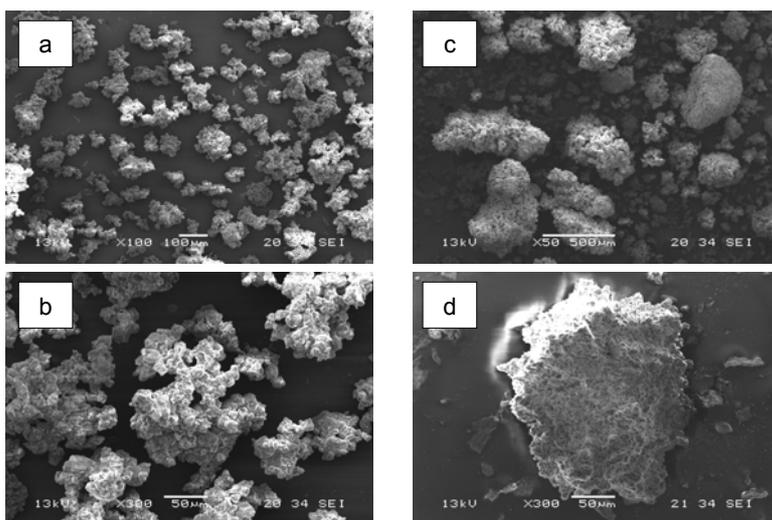


Figure 2: SEM images of the Li_4SiO_4 sorbent doped with 30 wt% of K_2CO_3 (a) and 30 wt% of $\text{K}_2\text{CO}_3/\text{Li}_2\text{CO}_3$ (c) before CO_2 sorption and the same samples (b and d, respectively) heated to 580°C in N_2 and quenched in N_2 to room temperature.

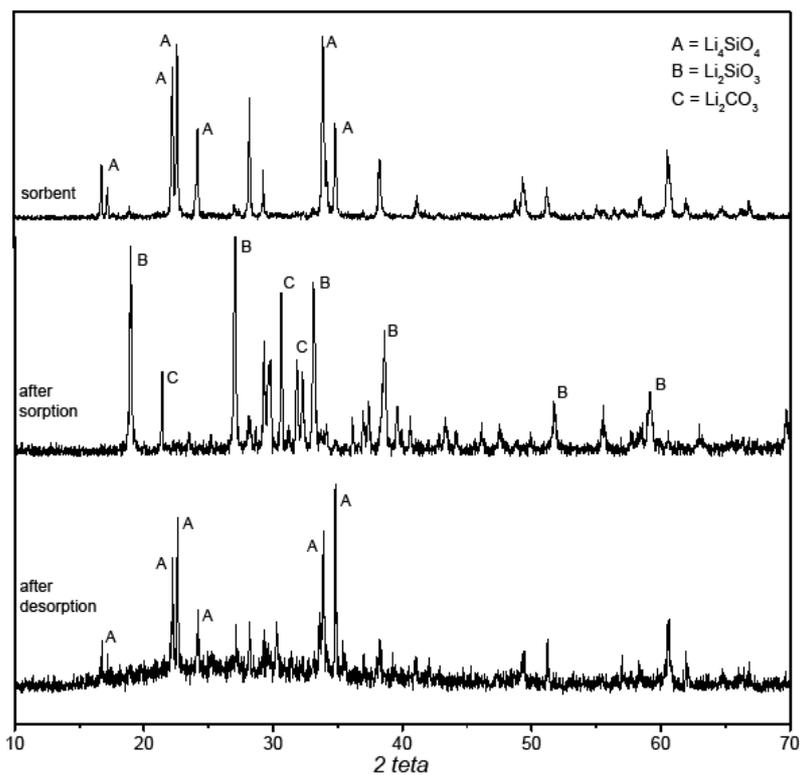


Figure 3: XRD patterns of Li_4SiO_4 sorbent with addition of 30 wt% of K_2CO_3 before (top) and during (middle) CO_2 sorption and after CO_2 desorption (bottom).

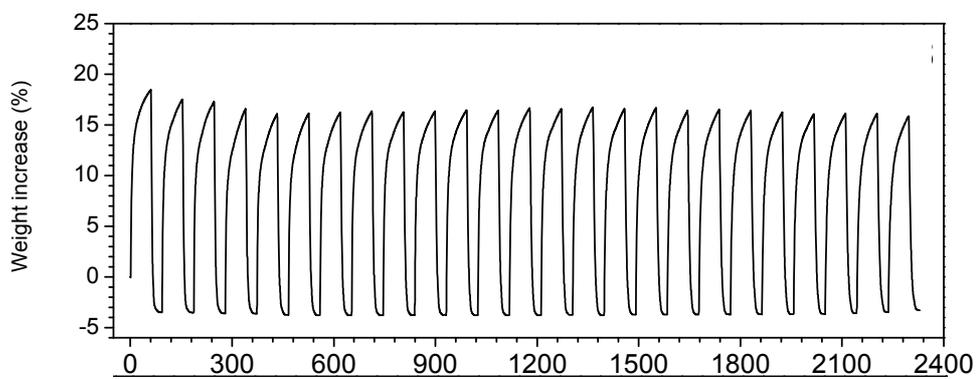


Figure 4: Multiple cycles of CO_2 sorption (60 min at 580 °C in 4 vol% CO_2) and desorption on the Li_4SiO_4 sorbent doped with 30 wt% of K_2CO_3 .

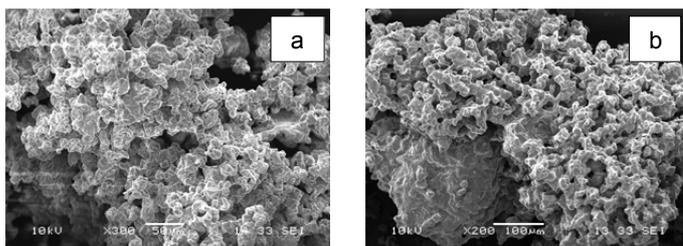


Figure 5: SEM images of the Li_4SiO_4 sorbent doped with 30 wt% of K_2CO_3 regenerated after the first cycle (a) and the sorbent regenerated after 25 sorption/desorption cycles (b).

4. Conclusions

In this study, different promoted Li_4SiO_4 -based sorbents were prepared by addition of potassium carbonate and binary/ternary alkali (Li, K and Na) carbonate eutectic mixtures for carbon dioxide capture at high temperature and low CO_2 concentration. For each series of promoted samples, the CO_2 sorption uptake and the conversion increased with increasing the promoter amount due to a more efficient distribution of promoter on a larger surface area. The formation of a molten Li-K carbonate shell on the surface of Li_4SiO_4 particles during the carbonation reaction improved significantly the CO_2 sorption rate. These results indicate that CO_2 sorption process is governed by the diffusion of CO_2 within the outer layer of the solid product Li_2CO_3 shell. The addition of 30 wt% of K_2CO_3 produced modified Li_4SiO_4 -based sorbents which provided the highest CO_2 sorption capacities after 2h at 580 °C (about 230 mg of CO_2 /g sorbent corresponding to a conversion of 80%). Besides, this sorbent maintained its sorption properties after 25 sorption/desorption cycles, displaying a good prospect for application in the separation at high temperatures of CO_2 from fuel-fired power stations as well as in the in situ removal of CO_2 produced in some reactions such as SMR and WGS reactions to enhance hydrogen production.

References

- Chavez R.H., Guadarrama J.J., 2011, Optimized process from post-combustion CO_2 capture in thermoelectric power plant using structured packing, *Chemical Engineering Transactions*, 25, 69-74.
- Kato M., Yoshikawa S., Nakagawa K., 2002, Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations, *Journal of Materials Science Letters*, 21(6), 485-487.
- Kato M., Nakagawa K., Essaki K., Maezawa Y., Takeda S., Kogo R., Hagiwara Y., 2005, Novel CO_2 absorbents using lithium-containing oxide, *International Journal of Applied Ceramic Technology*, 2(6), 467-475.
- Ochoa-Fernández E., Rønning M., Grande T., Chen D., 2006, Synthesis and CO_2 capture properties of nanocrystalline lithium zirconate, *Chemistry of Materials*, 18, 6037-6046.
- Pannocchia G., Puccini M., Seggiani M., Vitolo S., 2007, Experimental and modelling studies on high temperature capture of CO_2 using lithium zirconate based sorbents, *Industrial & Engineering Chemistry Research*, 46, 6697-6706.
- Pires J.C.M., Martins F.G., Alvim-Ferraz M.C.M., Simões M., 2011, Recent developments on carbon capture and storage: An overview, *Chemical Engineering Research and Design* 89, 1446-1460.
- Seggiani M., Puccini M., Vitolo S., 2011, High-Temperature and Low Concentration CO_2 Sorption on Li_4SiO_4 based Sorbents: Study of the used silica and doping method effects, *International Journal of Greenhouse Gas Control*, 5, 741-748.
- Seggiani M., Puccini M., Vitolo S., 2013, Alkali promoted lithium orthosilicate for CO_2 capture at high temperature and low concentration, *International Journal of Greenhouse Gas Control*, in press, DOI: 10.1016/j.ijggc.2013.04.009.
- Soundararajan R., Gundersen T., 2012, Coal based power plants using oxy-combustion for CO_2 capture: pressurized coal combustion to reduce capture penalty, *Chemical Engineering Transactions*, 29, 187-192.
- Wang J., Manovic V., Wu Y., Anthony J., 2010, CaO-based sorbents for capturing CO_2 in clean energy processes, *Chemical Engineering Transactions*, 21, 187-192.
- White C.M., Strazisar B.R., Granite E.J., Hoffman J.S., Pennline H.W., 2003, Separation and capture of CO_2 from large stationary sources and sequestration in geological formations - coal beds and deep saline aquifers, *Journal of Air Waste Management Association* 53, 645-715.
- Yang H., Xu Z., Fan M., Gupta R., Slimane R.B., Bland A.E., Wright I., 2008, Progress in carbon dioxide separation and capture: A review, *Journal of Environmental Sciences* 20, 14-27.